A Comprehensive Study on the Mechanical and Thermal Properties of Nanoclay Reinforced Polymers at Various Temperatures*†

Selen Bayar, Ph.D. Student, Major: Mechanical Engineering
Mentor: Feridun Delale, Prof., Mechanical Engineering

ABSTRACT:
In this study, the mechanical and thermal properties of nanoclay reinforced polymer resins are investigated at various temperatures. The effect of nanoclay reinforcement was elicited by varying its weight percentage from 0% to 10% in the polymer. Three different polypropylene (PP) resins were studied. The temperature was varied from -65°F (-54ºC) to 160°F (71ºC). To predict the experimental results a micromechanical model based on the Mori-Tanaka formulation was developed. The results indicate that the addition of nanoclay to PP leads to a stronger and stiffer nanocomposite. It was also found that the strength and stiffness of PP are drastically reduced at higher temperatures. However, nanoclay reinforcement somewhat mitigates this deterioration. The comparison of the theoretical and experimental results indicates that the Mori-Tanaka formulation may be a useful tool to predict these mechanical properties.

KEYWORDS: Polymers, nanoclay, nanocomposites, high temperature, low temperature, mechanical and thermal properties.

I. INTRODUCTION

In recent years there has been heightened interest in developing nanoclay reinforced composites due to their improved performance at high temperatures under various loading conditions, including impact [1-9]. It is believed that the reinforcement of thermoset and thermoplastic polymers with nanoclay may improve not only the strength and stiffness of the material, but also fire retardancy and smoke toxicity, thus providing better protection to personnel in civilian and military vehicles. The aim of this research project is to conduct a comprehensive study to determine the properties of nanoclay reinforced thermoplastic and thermoset polymers under various loading conditions, including impact, by varying the nanoclay reinforcement from 0% to 10% and the temperature from -65°F (-54ºC) to 160°F (71ºC). To elicit the effect of resin, three different resins are tested under tensile and impact loads. Nanoclay reinforced epoxy specimens also are studied. To predict the experimental results a micromechanics model supplemented with Finite Element calculations is being developed.

II. THE EXPERIMENTAL WORK

The tensile testing undertaken under this research has two distinct goals: a) to determine the effect of nanoclay reinforcement and temperature on the mechanical and thermal properties of nanoclay reinforced polymers and b) to use the obtained baseline data in impact analysis of the resulting composites. First, ASTM standard Type I dog-bone shaped polypropylene (PP) resin specimens reinforced with varying weight fractions of nanoclay (0%, 1%, 3%, 6% and 10%), of which some were instrumented with strain gages, were subjected to tensile loads and the stress-strain curves were obtained to determine the mechanical and thermal properties of the nanocomposite. Next the specimens were tested at various temperatures, from -65°F (-54ºC) to 160°F (71ºC), to elicit the effect of temperature. The effect of resin was also studied by using 3 different PP resins. For each data point at least 5 specimens were tested.

Even though we have extensive experimental data (to date more than 120 specimens were tested). Due to space limitation here we present some representative results to depict our findings. Figure 1 shows the effect of increased nanoclay reinforcement on the mechanical properties of the resulting nanocomposite.

* This work was supported by US ARMY – TARDEC under contract #W56HZV-09-C-0569

† UNCLASSIFIED: Dist A. Approved for public release

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **04 MAR 2010**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **A Comprehensive Study on the Mechanical and Thermal Properties of Nanoclay Reinforced Polymers at Various Temperatures**	5a. CONTRACT NUMBER **W56HZV-09-C-0569**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Selen Bayar**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000, USA**	8. PERFORMING ORGANIZATION REPORT NUMBER **20608**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) **TACOM/TARDEC**
	11. SPONSOR/MONITOR’S REPORT NUMBER(S) **20608**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT
In this study, the mechanical and thermal properties of nanoclay reinforced polymer resins are investigated at various temperatures. The effect of nanoclay reinforcement was elicited by vary-ing its weight percentage from 0% to 10% in the polymer. Three different polypropylene (PP) resins were studied. The temperature was varied from -65°F (-54ºC) to 160°F (71ºC). To predict the experimental results a micromechanical model based on the Mori-Tanaka formulation was developed. The results indicate that the addition of nanoclay to PP leads to a stronger and stiffer nanocomposite. It was also found that the strength and stiffness of PP are drastically reduced at higher temperatures. However, nanoclay reinforcement somewhat mitigates this de-terioration. The comparison of the theoretical and experimental results indicates that the Mori-Tanaka formulation may be a useful tool to predict these mechanical properties.

15. SUBJECT TERMS
Polymers, nanoclay, nanocomposites, high temperature, low temperature, me-chanical and thermal properties

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**SAR**	**4**	

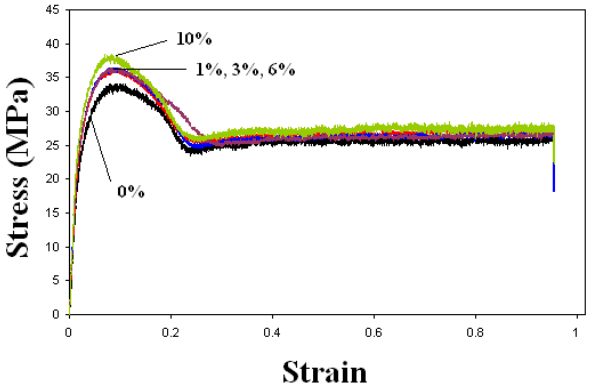

Figure 1. Effect of nanoclay reinforcement

As the weight percentage of nanoclay increases from 1% to 10% the ultimum stress and the stiffness of the material increase perceptibly. It must be noted that PP based nanocomposites display significant deformation before failure (more than 100%). Figure 2 depicts the effect of temperature on the properties of PP with 1% nanoclay reinforcement.

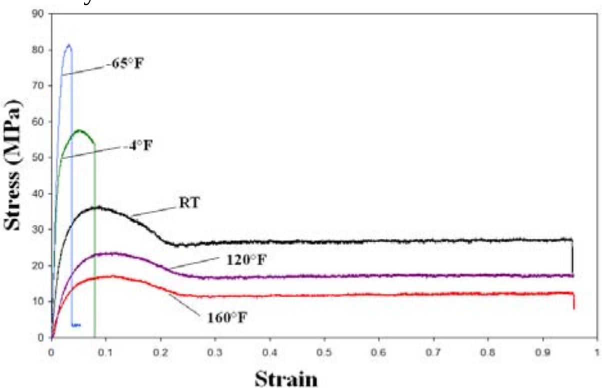

Figure 2. Effect of temperature on PP specimens reinforced with 1% nanoclay

It is first noted at the higher temperatures the strength and stiffness are significantly reduced compared with those at room temperature. Whereas at lower temperatures the material stiffens, has higher strength and fails at relatively low strains. Similar behaviour is also observed at higher percentages of nanoclay reinforcement. However, the deterioration of properties observed at higher temperatures is somewhat mitigated by the addition of higher percentages of nanoclay. For example, as seen in Figure 3, at 120°F an increase in the percentage of nanoclay reinforcement leads to higher stiffness and strength for the resulting nanocomposite.

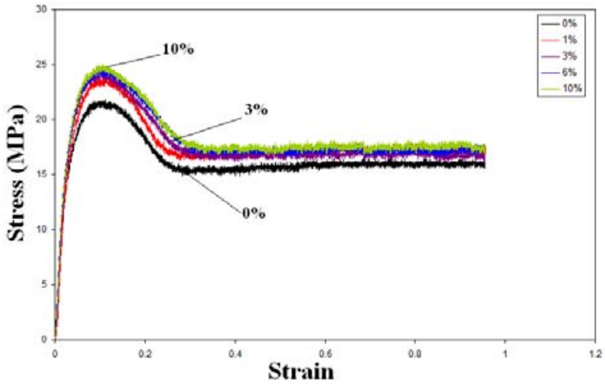

Figure 3. Effect of reinforcement at high temperature (120ºF)

Next specimens with three different PP formulations and the same 3% nanoclay reinforcement were subjected to tensile loading at room, high and low temperatures. The results for room temperature shown in Figure 4 indicate that the PP resin formulation may have drastic effects on the properties of the nanocomposite, especially failure elongation.

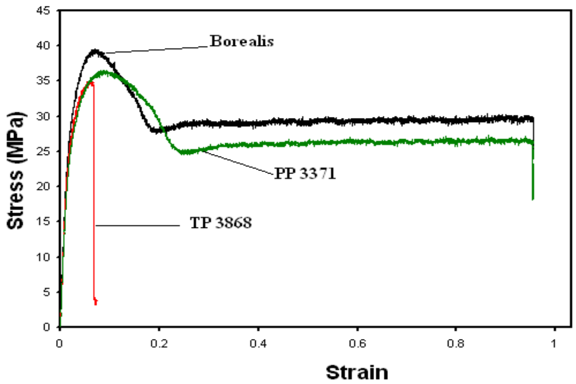

Figure 4. Effect of different resins with 3% nanoclay reinforcement

Some of the results for nanoclay reinforced PP specimens are also summarized in Table 1. The results indicate that with increasing nanoclay reinforcement the Young's Modulus and ultimate stress increase perceptibly.

Temperature	Nanoclay Reinforced	E_1 (GPa)	Ult. Stress (MPa)	Strain at Ult. Stress	Necking Stress (MPa)	End of Test Strain
Room Temperature	0%	1.285	33.044	0.098	24.805	0.954
	1%	1.489	35.346	0.091	26.071	0.954
	3%	1.557	35.096	0.094	25.392	0.953
	6%	1.616	35.590	0.092	25.751	0.954
	10%	1.809	36.584	0.089	26.160	0.953
120°F (49°C)	0%	0.743	21.678	0.105	15.330	0.956
	1%	0.748	23.209	0.108	16.613	0954
	3%	0.811	23.952	0.108	16.793	0.954
	6%	0.857	24.537	0.108	17.040	0.953
	10%	0.878	24.717	0.110	17.041	0.955
160°F (71°C)	0%	0.403	14.542	0.130	10.378	0.957
	1%	0.499	15.803	0.121	11.188	0.957
	3%	0.480	16.141	0.117	11.210	0.957
	6%	0.519	16.433	0.113	11.143	0.955
	10%	0.531	16.883	0.110	11.413	0.954

Table 1. Properties obtained experimentally for nanoclay reinforced PP specimens

III. Modeling and Numerical Results

To predict the properties obtained experimentally, a micomechanics model based on the Mori-Tanaka formulation [10] was developed. The Mori-Tanaka Model is based on micromechanics and uses Eshelby's solution for inclusions embedded in an infinite matrix. Here we approximate the nanoclay flakes as thin disks with the aspect ratio α calculated as the thickness to length ratio. Referring to [10], the normalized Young's modulus of the nanocomposite can be expressed as:

$$\frac{E_1}{E_m} = \frac{1}{1 + c(A_1 + 2\nu_m A_2)A} \qquad (1)$$

where, E_1 and E_m are the Young's moduli of the composite and the matrix respectively, c is the volume fraction of nanoclay and the coefficients A_1, A_2 and A are given by:

$$A_1 = D_1\left(B_4 + B_5\right) - 2B_2 \qquad (2)$$

$$A_2 = \left(1 + D_1\right)B_2 - \left(B_4 + B_5\right) \qquad (3)$$

and

$$A = 2B_2B_3 - B_1\left(B_4 + B_5\right) \qquad (4)$$

where

$$B_1 = cD_1 + D_2 + \left(1-c\right)\left(D_1S_{1111} + 2S_{2211}\right) \qquad (5)$$

$$B_2 = c + D_3 + \left(1-c\right)\left(D_1S_{1122} + S_{2222} + S_{2233}\right) \qquad (6)$$

$$B_3 = c + D_3 + \left(1-c\right)\left[S_{1111} + \left(1 + D_1\right)S_{2211}\right] \qquad (7)$$

$$B_4 = cD_1 + D_2 + \left(1-c\right)\left(S_{1122} + D_1S_{2222} + S_{2233}\right) \qquad (8)$$

$$B_5 = c + D_3 + \left(1-c\right)\left(S_{1122} + S_{2222} + D_1S_{2233}\right) \qquad (9)$$

and

$$D_1 = 1 + 2\left(\mu_p - \mu_m\right)\Big/\left(\lambda_p - \lambda_m\right) \qquad (10)$$

$$D_2 = \left(\lambda_m + 2\mu_m\right)\Big/\left(\lambda_p - \lambda_m\right) \qquad (11)$$

$$D_3 = \lambda_m\Big/\left(\lambda_p - \lambda_m\right) \qquad (12)$$

The *D* terms are defined by using μ_m, λ_m and μ_p, λ_p, which are the Lame constants of the matrix and inclusions, respectively. In the *B* terms, the components of Eshelby's tensor S_{ijkl} given below are used:

$$S_{1111} = \frac{1}{2\left(1-\nu_m\right)}\left\{1 - 2\nu_m + \frac{3\alpha^2 - 1}{\alpha^2 - 1} - \left[1 - 2\nu_m + \frac{3\alpha^2}{\alpha^2 - 1}\right]g\right\} \qquad (13)$$

$$S_{2222} = S_{3333} = \frac{3}{8\left(1-\nu_m\right)}\frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4\left(1-\nu_m\right)}\left[1 - 2\nu_m - \frac{9}{4\left(\alpha^2 - 1\right)}\right]g \qquad (14)$$

$$S_{2233} = S_{3322} = \frac{1}{4\left(1-\nu_m\right)}\left\{\frac{\alpha^2}{2\left(\alpha^2 - 1\right)} - \left[1 - 2\nu_m + \frac{3}{4\left(\alpha^2 - 1\right)}\right]g\right\} \qquad (15)$$

$$S_{2211} = S_{3311} = -\frac{1}{2\left(1-\nu_m\right)}\frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4\left(1-\nu_m\right)}\left\{\frac{3\alpha^2}{\alpha^2 - 1} - \left(1 - 2\nu_m\right)\right\}g \qquad (16)$$

$$S_{1122} = S_{1133} = -\frac{1}{2\left(1-\nu_m\right)}\left[1 - 2\nu_m + \frac{1}{\alpha^2 - 1}\right] + \frac{1}{2\left(1-\nu_m\right)}\left[1 - 2\nu_m + \frac{3}{2\left(\alpha^2 - 1\right)}\right]g \qquad (17)$$

$$S_{2323} = S_{3232} = \frac{1}{4\left(1-\nu_m\right)}\left\{\frac{\alpha^2}{2\left(\alpha^2 - 1\right)} + \left[1 - 2\nu_m - \frac{3}{4\left(\alpha^2 - 1\right)}\right]g\right\} \qquad (18)$$

$$S_{1212} = S_{1313} = \frac{1}{4\left(1-\nu_m\right)}\left\{1 - 2\nu_m - \frac{\alpha^2 + 1}{\alpha^2 - 1} - \frac{1}{2}\left[1 - 2\nu_m - \frac{3\left(\alpha^2 + 1\right)}{\alpha^2 - 1}\right]g\right\} \qquad (19)$$

Here ν_m is the Poisson's ratio of the matrix. In Eshelby's tensor, the *g* term has two different expressions depending on the aspect ratio α of the inclusion:

$$g = \frac{\alpha}{\left(\alpha^2 - 1\right)^{3/2}}\left\{\alpha\left(\alpha^2 - 1\right)^{1/2} - \cosh^{-1}\alpha\right\};\ \alpha > 1 \qquad (20)$$

$$g' = \frac{\alpha}{\left(1 - \alpha^2\right)^{3/2}}\left\{\cos^{-1}\alpha - \alpha\left(1 - \alpha^2\right)^{1/2}\right\};\ \alpha < 1 \qquad (21)$$

In the calculations, for the matrix and the nanoclay the following material and geometric properties are used:

Matrix: Polypropylene

- E_m = 1.222 GPa (average experimental result)
- ν_m = 0. 35 (assumed)
- V_m = unknown (volume fraction of matrix)
- W_m = weight fraction of matrix
- γ_m = 8829N/m^3 (specific weight of matrix)
- μ_m = 74 GPa (calculated)
- λ_m = 172.8 GPa (calculated)

Particle: Nanoclay

- E_p = 200 GPa (assumed; from molecular dynamics calculations)
- ν_p = 0. 35 (assumed)
- $c=V_p$ = unknown (volume fraction of nanoclay)
- W_p = weight fraction of nanoclay
- γ_p = 18,639 N/m^3 (specific weight of nanoclay)
- μ_p = 0.453 Gpa (calculated)
- λ_p = 1.056 Gpa (calculated)

First, we calculate the volume fraction of nanoclay to be able to use the Mori-Tanaka formulation. The volume fraction of nanoclay in terms of the weigth fraction can be written as:

$$c = V_p = \frac{W_p / \gamma_p}{W_p / \gamma_p + \left(1 - W_p\right) / \gamma_m} \qquad (22)$$

For each nanoclay reinforcement, the volume fraction of nanoclay is obtained as:

Weight fraction of nanoclay	Volume fraction of nanoclay
1%	0.0048
3%	0.0144
6%	0.0293
10%	0.0500

Table 2. The volume fraction of nanoclay

To determine the aspect ratio of nanoclay flakes, we use for thickness $d_s = 0.615$ nm and for diameter a= 200 nm. Thus, the aspect ratio of nanoclay can be calculated as: $\alpha = d_s/a$ =0.003075. Since the aspect ratio of nanoclay is smaller than 1, we use g' in Eshelby's tensor. The calculations for various weight fractions (converted to volume fractions) were performed using commercial software. Comparison of the theoretical predictions and experimental results at room temperature for the E_1/E_mratio is shown in Figure 5. The preliminary results indicate that the Mori-Tanaka formulation can be a useful tool in predicting the Young's modulus of the nanocomposite.

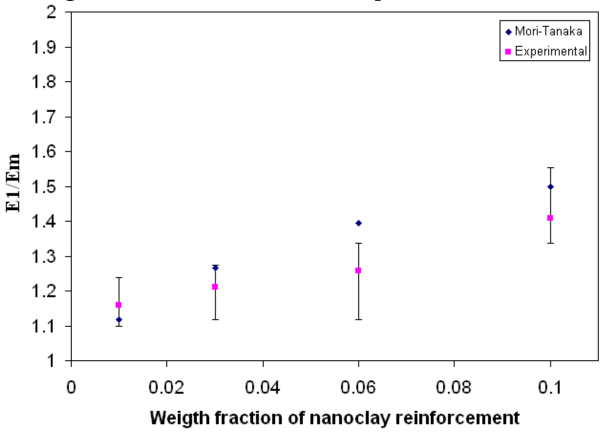

Figure 5. Comparison of Mori-Tanaka end experimental results at room temperature for nanoclay reinforced PP

IV. CONCLUSIONS

In this study the mechanical and thermal properties of three PP resins reinforced with nanoclay particles were studied at room, elevated and low temperatures. From the results obtained so far, the following conclusions can be deduced:

1. Nanoclay reinforcement improves the mechanical properties of PP resins. The strength and stiffness of the resulting nanocomposite increase as the percentage of nanoclay reinforcement increases
2. The choice of the PP resin can have a significant effect on the behavior of the nanocomposite, especially the failure strain
3. At higher temperatures the mechanical properties of PP deteriorate. However, the addition of nanoclay somewhat mitigates this deterioration
4. At low temperatures, the material stiffens, has higher ultimate stress and fails at comparatively low strains
5. The Mori-Tanaka model may be a useful tool in predicting the Young's modulus of the nanocomposite.

ACKNOWLEDGMENTS

This work was supported by US. Army – TARDEC under contract #W56HZV-09-C-0569. I would like to thank my mentor Prof. Feridun Delale for his guidance and support. Special thanks are due to Dr. Jerry Chung and Mr. Matthew Dabrowski of Novus Technologies Corporation who provided the nanocomposite specimens. Also, I am grateful for the guidance and help provided by Profs. Benjamin Liaw and Jackie Li. The feedback provided by Mr. Ramki Iyer and Dr. Basavaraju Raju of TARDEC prior to publication is greatly appreciated.

REFERENCES

[1] A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito. J. Mater. Res. 1993;8:1179.

[2] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito. J. Mater. Res. 1993;8:1185

[3] J.W. Gilman. Appl. Clay Sci. 1999;15:31.

[4] Z. Wang and T.J. Pinnavaia. Chem. Mater. 1998;10:3769.

[5] S.D. Burnside and E.P. Giannelis. J. Polym. Sci. Phys. 2000;38:1595.

[6] C.S. Triantafillidis, P.C. LeBaron and T.J. Pinnavaia. J. Solid State Chem. 2002;167:354.

[7] D. Ratna, N.R. Manoj, R. Varley, R.K. Singh Raman and G.P. Simon. Polym. Int. 2003;167:354.

[8] N. Sheng, M.C. Boyce, D.M. Parks, G.C. Rutledge, J.I. Abes and R.E. Cohen. J. Polymer 2003;45:487.

[9] F. Hussain, M/ Hojjati, M. Okamoto and R. E. Gorga. J. Composite Materials 2006;40:1511.

[10] G.P. Tandon and G.J. Weng. J. Polymer Comp. 1984;5:327.